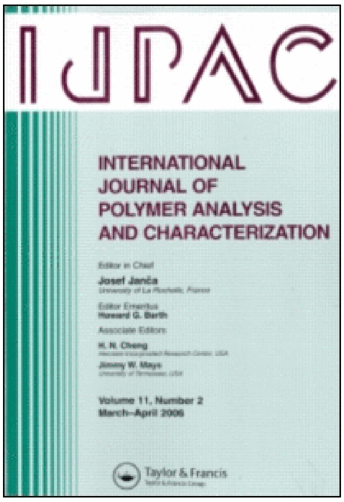

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Growth Behavior and Characterization of Poly(o-toluidine-co-m-bromoaniline) by Cyclic Voltammetry

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Electrochemical copolymerization of o-toluidine (OT) with m-bromoaniline (MBA) was carried out in 1M HCl by cyclic voltammetry. Polymeric films were deposited by employing different conditions such as cycle number and feed ratio of comonomers. Electrochemical homopolymerization of OT and MBA was also done independently. A growth equation for copolymer deposition relating the parameters of operation and charge associated for film deposition was obtained. The copolymer was also prepared using potassium peroxodisulfate as an oxidizing agent. The chemically and electrochemically synthesized copolymer was characterized through FT-IR and UV-visible spectroscopic studies.

Keywords: Copolymerization; m-bromoaniline and o-toluidine; Cyclic voltammetry; Growth equation; Characterization

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Polyaniline (PANI) is one of the most studied polymers among conducting polymers. Its unique properties, like ease of preparation in an aqueous medium, good stability in air[1], simplicity in the doping process[2], good electronic properties[3], electro-chromic effects[4], well-behaved electrochemistry[5–7], and moderately high conductivity in the doped form[8, 9], have made it a candidate of great technological promise.

PANI and its derivatives can be synthesized by either chemical or electrochemical oxidation of aniline as a bulk powder or as thin films on electrodes. Electrochemical techniques for the synthesis of PANI by anodic oxidation of aniline include potentiostatic, galvanostatic, and potential cyclic (cyclic voltammetry) methods.

More detailed cyclic voltammetric studies of the synthesis and electrochemistry of alkyl ring-substituted polyanilines have been reported by several workers[3, 10]. They also prepared copolymers by chemical and electrochemical methods using aniline as the parent monomer and alkyl ring-substituted anilines as comonomers. By varying the fraction of comonomers in the feed, the electrical conductivities of the copolymers could be in a broad range of ca. $0.1–10\,\mathrm{S\,cm^{-1}}$ after doping[11]. Leclerc et al.[12] have prepared poly (alkyl anilines) through electrochemical synthesis by cyclic voltammetry and found that the alkyl substituents modify the polymerization reaction. Later, Ye et al.[13] prepared soluble and conductive poly(aniline-co-N-butyl aniline) by an electrochemical method and proposed that the copolymer had random distribution of comonomers as polymerization was initiated by the electrochemical oxidation of both comonomers.

Furthermore, in order to improve the processability of PANI, various copolymers of PANI have also been synthesized[14] and their properties studied. Among these copolymers, ring-substituted PANIs such as polytoluidines, polyanisidines, and polyphenetidines were found to be significantly more soluble than the unsubstituted PANI[15] in N-methyl pyrrolidone (NMP). They are also soluble in less polar solvents such as chloroform and toluene. Ring-substituted PANIs, however, are less conducting than the unsubstituted PANI.[16] Choi et al.[17] have reported the rheological properties of poly(aniline-co-o-ethoxy aniline) synthesized by chemical methods. Kilmartin et al.[18] have studied typical cyclic voltammetric studies and explained the spectroscopic and photoelectrochemical behavior of several substituted aniline-based copolymers.

Electrochemical copolymerization of aniline derivatives with para-phenylene diamine in aqueous sulfuric acid media has been investigated using cyclic voltammetry[19]. Copolymers of aniline with 3,4-dihydroxybenzoic acid[20] and 2,5-aniline disulfonic acid[21] have also been synthesized by electrochemical polymerization. The results on the copolymerization of 2,5-diaminobenzene sulfonic acid and para-phenylene diamine revealed better stability for the film of the latter system[22]. Copolymerization of aniline with other conducting film-forming monomers was investigated to improve the properties of aniline- based copolymer[23].

Freestanding films of PANI have been studied for applications where the reversible doping characteristics of the polymer are used to affect morphological changes in the polymer film, which then impart permeation properties to the membrane[24, 25]. Kim et al.[26] have used halomethyl-substituted polyimides to improve the separation of gases through polyimide membranes and postulated that the halo substitution might enhance the solubility of oxygen in these membranes[27]. In order to investigate this concept, polymerizations of substituted anilines involving alkyl group functionalization were made[28]. However, very little research has been focused on the effect of functionalizing aniline with a hydrophobic, electron-withdrawing group such as halogens before polymerization. Dao et al.[29] and Snauwaeri et al.[30] synthesized poly(2-fluoroaniline) by electrochemical and chromic acid oxidation. Later, Kwon et al.[31] studied the spectral characteristics and thermal behavior of the chemically prepared polyfluoroalkanes.

A new dimension in fundamental studies on the polymerization and growth properties of polyaniline-employing electrochemical techniques has been opened up by Stilwell and Park[32]. They conducted a study on the film growth characteristics of polyaniline films grown by the potential cycling method. Polymer growth rates have been determined as a function of monomer concentration, number of cycles, and other conditions, and they confirmed by an analysis of their results that the oxidation products responsible for growth are surface bound species.

It was in the midst of these interesting developments that the current investigation was taken up. Copolymerization of o-toluidine (OT) with m-bromoaniline (MBA) was chosen for a detailed investigation on its polymer growth characteristics. Cyclic voltammetry was used to affect the simultaneous synthesis and characterization. A detailed literature search revealed that the use of m-bromoaniline as one monomer in copolymer formation has not been attempted so far. Recently, Rajendran et al.[33,34] have deduced the growth behavior of copolymer formation by performing polymerization of aniline with haloanilines through the pulse potentiostatic method. In the current study the growth behavior of deposition of copolymer based on OT and MBA was monitored under different conditions to deduce a growth equation. Cyclic voltammetry (CV) was also used for electrochemical characterization. The copolymer was characterized by FT-IR and UV-visible spectroscopic studies.

EXPERIMENTAL

Chemicals

O-toluidine (OT) and m-bromoaniline (MBA) were purchased from Fluka, Sigma-Aldrich, 9471 Buchs, Switzerland and USA, and used as received. Potassium peroxodisulfate (PDS) (E-Merck, Darmstadt, Germany) and dimethyl formamide (spectral grade, E-Merck, Darmstadt, Germany) were used as such.

Electrochemical Copolymerization

The electrochemical copolymerization was performed in a single compartment cell of 16 mL capacity, fitted with a Pt disc as working electrode, Pt wire as auxiliary electrode, and Ag/AgCl as reference electrode. The copolymer film was deposited electrochemically on the Pt disk electrode from 2 M aqueous HCl solutions of OT and MBA in a feed ratio represented as mole fraction of the feed (0.1) by reversibly cycling the potential in the range 0.1–1.0 V for 20 cycles at a scan rate of 50 mV/s or 100 mV/s. The cyclic voltammogram (CV) of the growing film of copolymer was recorded continuously and coincidentally with the synthesis.

Similar experiments were conducted using various feed ratios of o-toluidine, namely 0.2, 0.4, 0.5, 0.6, and 0.8 (feed ratios are expressed in terms of mole fractions of OT), and CVs of the growing films of the copolymers were recorded.

Electrochemical Homopolymerization of OT and MBA

The film of homopolymer was deposited electrochemically on the Pt electrode from 1 M HCl aqueous solution of the monomer (OT or MBA; 500 mM) using cyclic voltammetry in the potential range of 0.0–1.0 V vs. Ag/AgCl for 20 cycles at a scan rate of 50 mV/s.

Chemical Copolymerization of OT with MBA

Copolymer of OT with MBA was prepared by the oxidation of a mixture of a OT and MBA of appropriate comonomer feed ratio (1:1) using PDS as the oxidant in 1 M HCl. The following simple typical procedure for the preparation of poly(OT-co-MBA) was used.

A mixture containing OT and MBA (in the feed ratio of 1:1) as prepared in 200 mL of 1 M HCl was cooled below 273 K using a freezing mixture (ice and sodium chloride). A pre-cooled solution of PDS containing 1.16 g in 80 mL 1 M HCl was then added drop-wise to the mixture with stirring over a period of 20 min. The solution was further stirred for about an hour in the freezing mixture.

Chemical Homopolymerization of OT

The homopolymer of OT was also synthesized chemically by using the procedure analogous to the synthesis of ANI[6] with PDS as oxidant. A typical procedure is outlined here for the chemical synthesis of POT.

A solution (500 mM) prepared by dissolving 10.7 g OT in 200 mL of 1 M HCl was cooled below 273 K using the freezing mixture. A pre-cooled solution of PDS (250 mL) containing 1.08 g in 80 mL of 1 M HCl was then added drop-wise to the monomer solution with stirring over a period of 20 min. The solution was further stirred for 1 h in the freezing mixture. A dark green product was reprecipitated. The precipitate was filtered through a G3 sintered glass crucible and washed with 1 M HCl continuously until the filtrate was colorless. The acid-doped poly-(o-toluidine) (POT) was dried under vacuum for 48 h at room temperature.

Characterization of Copolymer

The following procedure was adopted for systematically studying the electrochemical characteristics of copolymer film. The copolymer film was deposited on the surface Pt electrode during the repetitive cycling of potential between 0.0 V and 1.0 V for poly(OT-co-MBA) at a scan rate of 50 mV/s from solution containing OT and MBA for various feed ratios.

The polymer coated electrode was placed in a monomer-free electrolyte (1 M HCl) and equilibrated by repetitive cycling of the potential in the range of 0.0–1.0 V until a constant CV pattern without any appreciable change in peak potentials or peak current values was obtained. Equilibration was achieved within a few cycles of potential scanning, indicating the stable structure of the film. The CV of the stabilized copolymer film was then recorded at various scan rates (20 mV/s, 50 mV/s, 100 mV/s, 200 mV/s, and 400 mV/s).

FT-IR Spectroscopy

FT-IR spectra of samples of homopolymer of OT and copolymer of poly(OT-co-MBA) samples were recorded using a Perkin-Elmer Fourier Transform Infrared spectrophotometer-1600 in the region 450–4000 cm^{-1} using KBr pellets.

UV-Visible Spectroscopy

UV-visible spectra of chemically prepared/bulk electropolymerized sample of OT and copolymer of poly(OT-co-MBA) were recorded in dimethyl formamide (DMF) using a UV-visible spectrophotometer (Shimadzu UV-PC2401, Japan).

RESULTS AND DISCUSSION

Electrochemical copolymerization of OT with MBA was carried out using cyclic voltammetry. For comparison, individual studies on homopolymerization of OT and MBA were also performed under conditions identical to those used for copolymerization.

Electropolymerization of MBA Through Cyclic Voltammetry

Figure 1 represents the CV for a solution (500 mM) of MBA recorded in 1 M HCl on a platinum electrode surface by cycling the potential between 0.0 V and 1.4 V vs. Ag/AgCl at a scan rate of 50 mV/s. Since the electro-oxidation of MBA occurs at a higher potential, the operating potential range with a higher switching potential of 1.4 V was required. An irreversible peak was observed in the first positive scan at 1.3 V with no corresponding cathodic response in the reverse scan.

Subsequent cycling of potential recorded in the potential range between −0.20 V and 1.0 V showed an irreversible anodic peak with E_p^a varying from 0.0–0.67 V to 0.70 V. The peak current values started decreasing with increase in the cycle number and the film. Hence, only an insulating film of poly(m-bromoaniline) (PMBA) was possible during the electropolymerization.

The CVs recorded for OT solutions of varying concentrations (100–500 mM) in 1 M HCl medium at constant scan rate showed two pairs of redox waves with peak potential values E_P^a (I) = 0.3 V and E_P^a (II) = 0.5 V. A typical CV is given in Figure 2.

Copolymerization of OT with MBA

Even when metabromoaniline as such does not show any promise for yielding an electroactive film on electropolymerization, there is a possibility that a simultaneous polymerization along with o-toluidine may yield a conducting polymeric film that would sustain a continuous synthesis on repeated cycling.

As the present investigation aims at performing the copolymerization of OT with MBA and critically comparing the results with those obtained

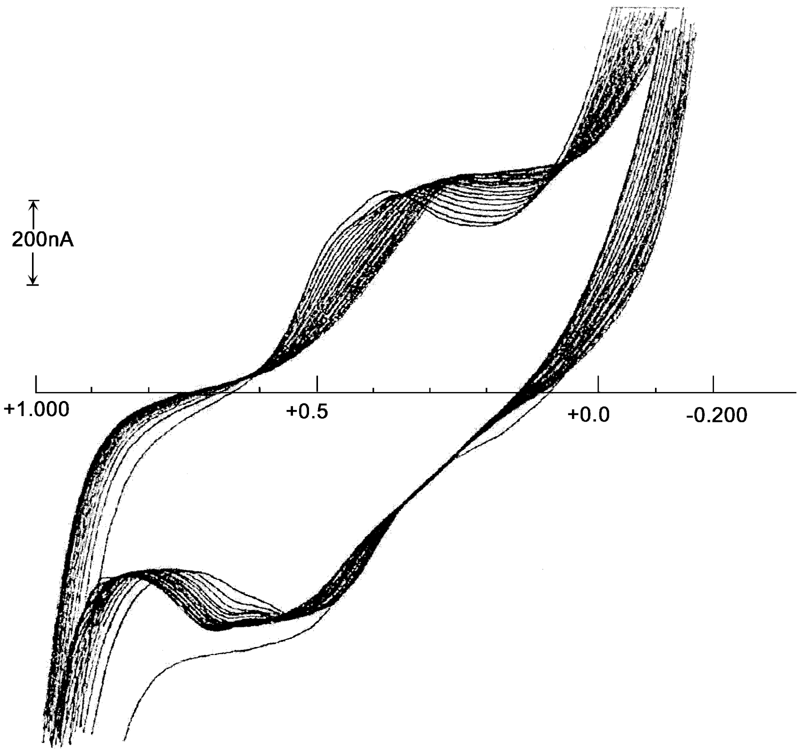


FIGURE 1 Cyclic voltammogram recorded during the polymerization of MBA. [MBA] = 500 mM; [HCl] = 1M; scan rate = 50 mV/s.

from homopolymerization of OT, attempts were made to electropolymerize OT in the presence of MBA using mixtures of these two monomers.

CVs were recorded during electropolymerization of mixtures of OT and MBA of varying feed ratios in 1 M HCl medium on a platinum electrode surface by cycling the potentials between −0.2 V and 1.0 V vs. Ag/AgCl at the scan rate of 50 mV/s. The total concentration of the two monomers OT and MBA was maintained at 500 mM in all cases.

Figures 3 and 4 represent the CVs recorded continuously for 20 cycles during the polymerization of OT with MBA for feed ratios of OT (i.e.) 0.1 and 0.9, at a scan rate of 50 mV/s. Apparently those CVs bear similarities to those recorded for polymerization of OT (Figure 2) as two redox pairs are found here. But a detailed analysis discloses the presence of significant differences with regard to peak positions, peak current values, and other growth characteristics.

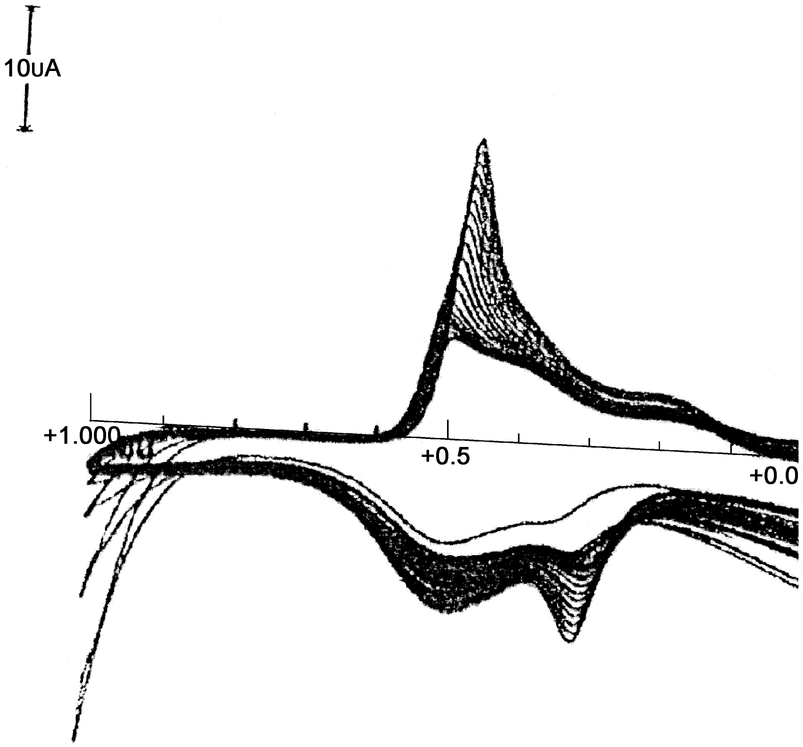


FIGURE 2 Cyclic voltammogram recorded during the polymerization of OT. [OT] = 250 mM; [HCl] = 1M; scan rate = 50 mV/s.

The first positive scan from a potential of −0.2 V showed the appearance of an anodic peak at ca. 0.5 V. This peak is attributed to the oxidation of OT as evident from Figure 2. The CV of MBA (I) has no anodic peak in this region.

In the second and subsequent cycles, the twin redox peaks were observed for the CVs of the higher feed ratio of OT. The first and second anodic peaks appear in the range 0.27–0.37 V and 0.44–0.54 V, respectively. The corresponding cathodic peaks with $E_p^c(I)$ and $E_p^c(II)$ appear in the range 0.33–0.38 V and 0.42–0.46 V, respectively. The peak separation of the two anodic processes or the cathodic process was found to be lower in comparison with the redox process as observed for homopolymerization of OT. The distinctive differences between the CVs for homopolymerization of OT and those for copolymerization of OT with MBA are discussed in the following sections.

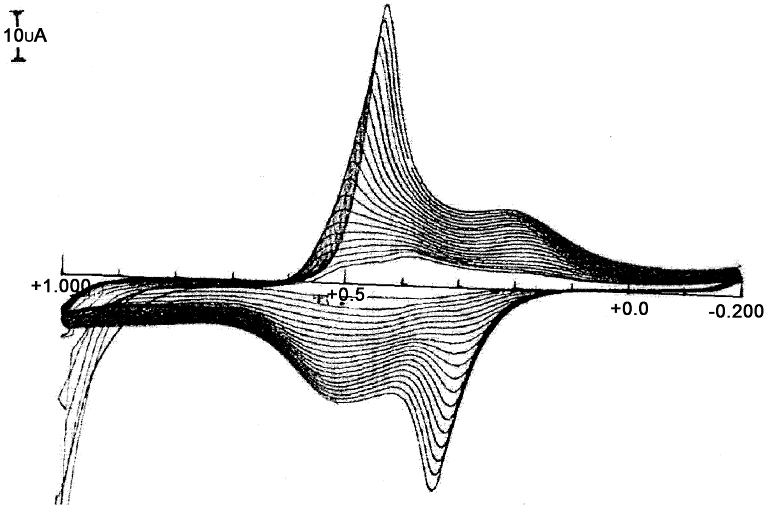


FIGURE 3 Cyclic voltammogram recorded during the copolymerization of OT with MBA. [OT] = 450 mM; [MBA] = 50 mM; [HCl] = 1M; scan rate = 50 mV/s.

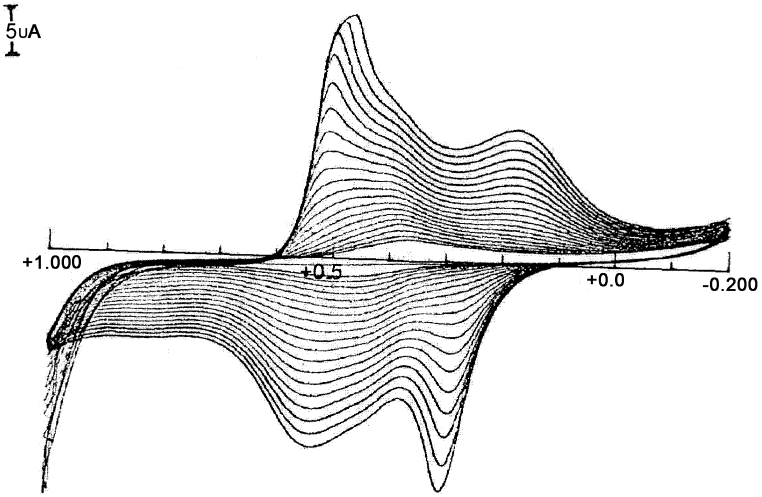


FIGURE 4 Cyclic voltammogram recorded during the copolymerization of OT with MBA. [OT] = 400 mM; [MBA] = 100 mM; [HCl] = 1M; scan rate = 50 mV/s.

The narrowing of the gap between the two peak potential values (both anodic and cathodic) is likely to arise from a tendency for the merging of the two oxidation processes, namely the leucoemeraldine type to the radical cation (semiquinone) and the conversion of the radical cation to the quinoidal structure. The resonance stabilization of the semiquinone radical ion state may be disturbed by the bromosubstitution and consequent steric effect of introducing non-coplanarity because of the bulky nature of the bromine atom. This bulkiness (Van der Waals radius 1.95 Å) may again hinder the formation of head-to-tail couplings. This may also give rise to branching chain in addition to linear chain polymerization. All these factors combine to destabilize the structure. From the results of Leclerc et al.[12] on the polymerization of o- and m-ethyl aniline (with the bulky ethyl group) it can be discerned that the peak potentials there also come nearer to each other. It is, however, difficult to disentangle the roles of electronic and steric effects in cases such as in this investigation.

Dependence of Peak Potentials on C_n and Feed Ratios of Monomers

The anodic peak potentials during the electropolymerization of OT and MBA using different feed ratios of the monomers at the scan rates of 50 mV/s for different cycle numbers, C_n (4, 8, 12, 16, and 20) are dependent on C_n and monomer feed ratios. E_p^a(I) and E_p^a(II) increase with cycle number for low feed ratios of OT. For high feed ratios of OT, the independent nature of E_p^a on C_n is observed. E_p^a(II) is found to increase with feed ratio of OT in contrast to the decreasing trend for E_p^a(I).

Dependence of Peak Current on C_n and Monomer Feed Ratios

The anodic peak current values are found to increase progressively with C_n for any fixed monomer feed ratio. An increasing trend is also observed for i_p^a values with increase in feed ratio of OT for any chosen value of C_n, which implies a decreasing trend with increase in feed ratio of MBA. However, a close comparison of all these values of i_p^a with the corresponding i_p^a values obtained for homopolymerization of OT reveals that these i_p^a values are very much less in all cases. Such differences become very significant for all high feed ratios of OT and for high C_n.

The reduced values of i_p^a and the fact that the CVs are not the superimposed CVs of the corresponding homopolymers indicate the formation of the copolymer, poly(OT-co-MBA), with simultaneous incorporation of MBA and OT units into the polymer chains. It is noteworthy that as in the case of homopolymerization of OT, the color of the medium does not change, indicating the nonformation of soluble oligomeric products during the deposition of the copolymer film.

The rate of copolymerization, $d(i_p^a)/dt$, as obtained from the slopes of the plots, i_p^a vs. C_n, was found to increase with increase in feed ratio of OT, which also indicates a consequent decrease with increase in feed ratio of MBA. In other words, the participation of MBA tends to retard the polymerization process.

Deducing the Growth Equation for Poly(OT-co-MBA) Deposition

Table I presents the anodic charges calculated for the various cycle numbers using the CVs recorded for the copolymerization with different feed ratios of OT and MBA. It was found that the anodic charge Q_G increases with increase in C_n for a fixed feed ratio of OT. In other words, Q_G exhibits a decreasing trend with increase in feed ratio of MBA for a fixed value of C_n.

In the present investigation, a correlation study on the growth of poly(OT-co-MBA) was carried out.

$$\text{Growth} = \text{charge}, \quad Q_G = k[\mathrm{OT}]^x[\mathrm{MBA}]^y(C_n)^z \qquad (1)$$

where k is the reaction rate constant for the deposition of the copolymer, poly(OT-co-MBA), and x, y, and z are the exponents of OT, MBA, and C_n, respectively. Equation (1) was proposed on the basis of a similar equation assigned for the kinetics of electrochemical polymerization of aniline[32] relating the growth of PANI with [AN] and C_n.

In order to determine the exact dependence of the growth of copolymer film on C_n, [OT], and [MBA], the following procedure was employed.

TABLE I Anodic charge values for different ratios of [OT] and [MBA] at various cycles; scan rate = 100 mV/s

	Charge Q (μC) for cycle number C_n				
Feed ratio of [OT]	4	8	12	16	20
0.1	1.12	2.20	3.25	4.32	5.30
0.2	2.28	4.53	6.75	8.98	11.2
0.3	5.25	10.4	15.6	20.7	25.8
0.4	7.13	14.2	21.3	28.4	35.4
0.6	9.55	19.1	28.5	38.0	47.5
0.8	18.0	35.89	53.8	71.7	89.6
0.9	28.7	57.2	85.0	111.5	142.5

The logarithmic form of Equation (1) was used for evaluating the exponents x, y, and z.

$$\log(\text{charge}) = \log \mathrm{k} + x \log[\mathrm{OT}] + y \log[\mathrm{MBA}] + z \log \mathrm{C_n} \tag{2}$$

For the determination of the dependence of growth on C_n, double logarithmic plots of the log(charge) vs. $\log C_n$ for a fixed monomers feed ratio (figure not shown) were made. The slopes of the plots are close to unity.

The dependence of growth on C_n was further verified by drawing direct plots of charge vs. cycle number for various feed ratios of OT and MBA (Figure 5). All these plots were found to be linear. This indicates a first power dependence of copolymer film growth on C_n.

Similar procedures could not be directly applied for the determination of exact growth on [OT] and [MBA], since both concentration terms are found to vary simultaneously while maintaining the feed ratios for any chosen value of C_n. By substituting any two experimentally determined anodic charge values Q_G corresponding to two different feed ratios of the monomers at a fixed C_n in the proposed equation (Equation 1), two equations were set up that were used to arrive at a simultaneous equation involving x and y terms.

Similarly, by choosing different sets of experimental values of Q_G corresponding to different sets of feed ratios of the monomers at the same fixed C_n, several pairs of simultaneous equations in x and y were set up. Solving these pairs of simultaneous equations for x and y, the average values of x and y were $+1.0$ and -0.5, respectively. This assignment of the values of x and y was further confirmed graphically by drawing suitable logarithmic and direct plots as described below.

For the evaluation of exponents of x and y, the logarithmic form of the proposed growth equation was used. In order to determine the dependence of growth on [OT], the plot between $\log(Q_G[\mathrm{MBA}]^{1/2})$ and log [OT] was drawn and found to have a slope value close to unity. The dependence of growth on [OT] was determined by drawing direct plots of $(Q_G[\mathrm{MBA}]^{1/2})$ vs. [OT] for fixed values of C_n (Figure 6, Plots A–E). All these plots were found to be linear with negligible intercept. Similarly, the dependence of growth on [MBA] was ascertained by using the graphically derived values of $+1.0$ for x in Equation (2). Logarithmic plots of $\log(Q_G/[\mathrm{OT}])$ vs. log[MBA] (figure not shown) were drawn for fixed values of C_n. The linearity of these plots showing slope values of nearly -0.5 confirms the inverse square root dependence of copolymer film growth on [MBA].

The value of y was further verified by drawing direct plots of $(Q_G/[\mathrm{OT}])$ vs. $[\mathrm{MBA}]^{-1/2}$ for different fixed values of C_n (Figure 7), which also showed linearity with negligible intercept. Making use of the values of x, y, and z thus determined from Figures 5, 6, and 7 and

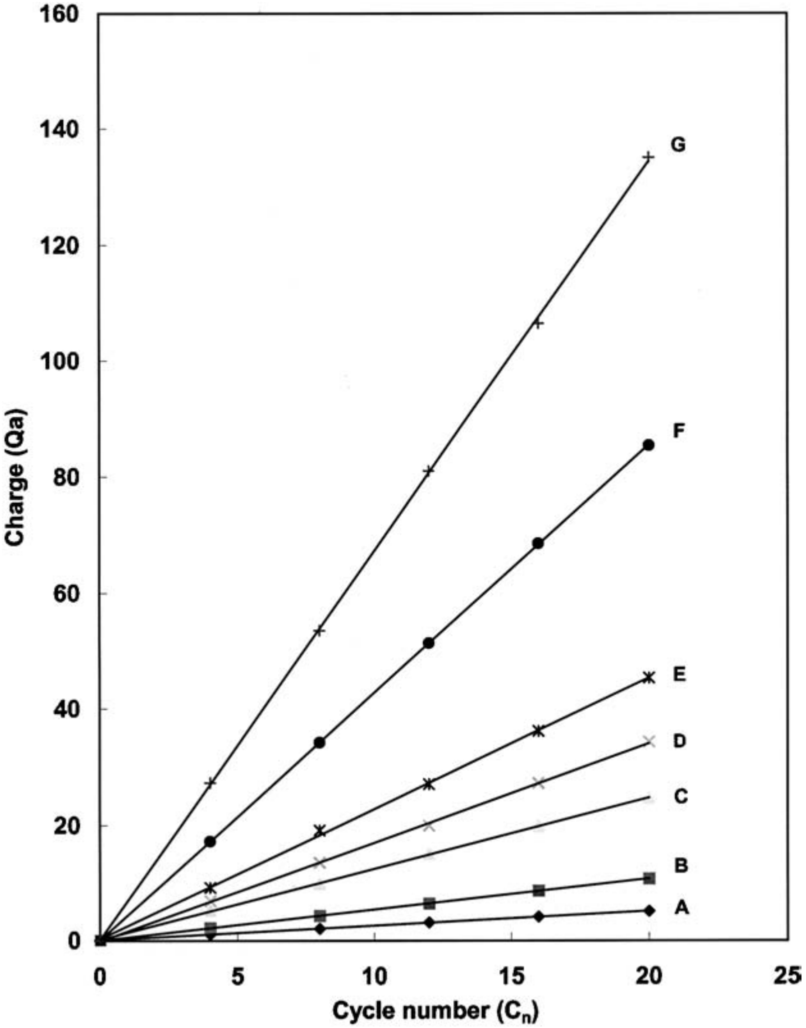


FIGURE 5 Effect of cycle number on charge for various [OT] and [MBA] during the copolymerization of OT with MBA; scan rate: 50 mV/s. Plot A: [OT] mM = 50, [MBA] mM = 450; Plot B: [OT] mM = 100, [MBA] mM = 400; Plot C: [OT] mM = 200, [MBA] mM = 300; Plot D: [OT] mM = 250, [MBA] mM = 250; Plot E: [OT] mM = 300, [MBA] mM = 200; Plot F: [OT] mM = 400, [MBA] mM = 100; Plot G: [OT] mM = 450, [MBA] mM = 50.

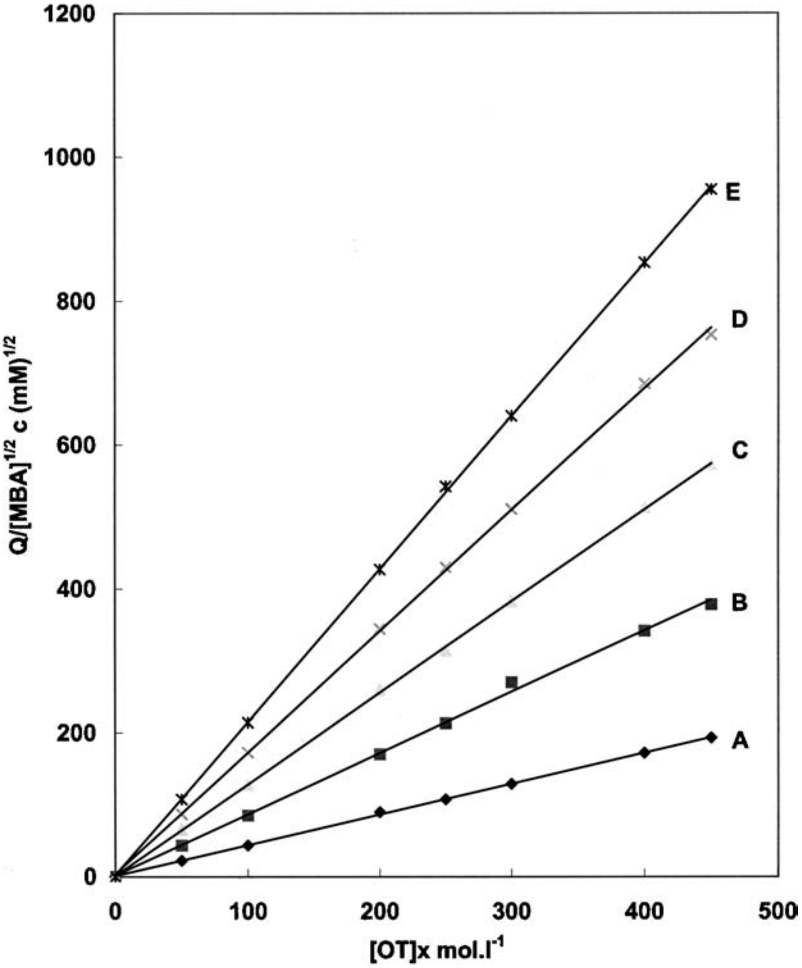


FIGURE 6 Effect of [OT] on charge for various cycle numbers during the copolymerization of OT with MBA; scan rate 50 mV/s. Plot A = cycle number 4; Plot B = cycle number 8; Plot C = cycle number 12; Plot D = cycle number 16; Plot E = cycle number 20.

applying the fact the linear plots pass through the origin with almost negligible intercept, the growth equation was finally deduced as

$$\text{Charge}\, Q_G = k\,[\text{OT}][\text{MBA}]^{-1/2}C_n \tag{3}$$

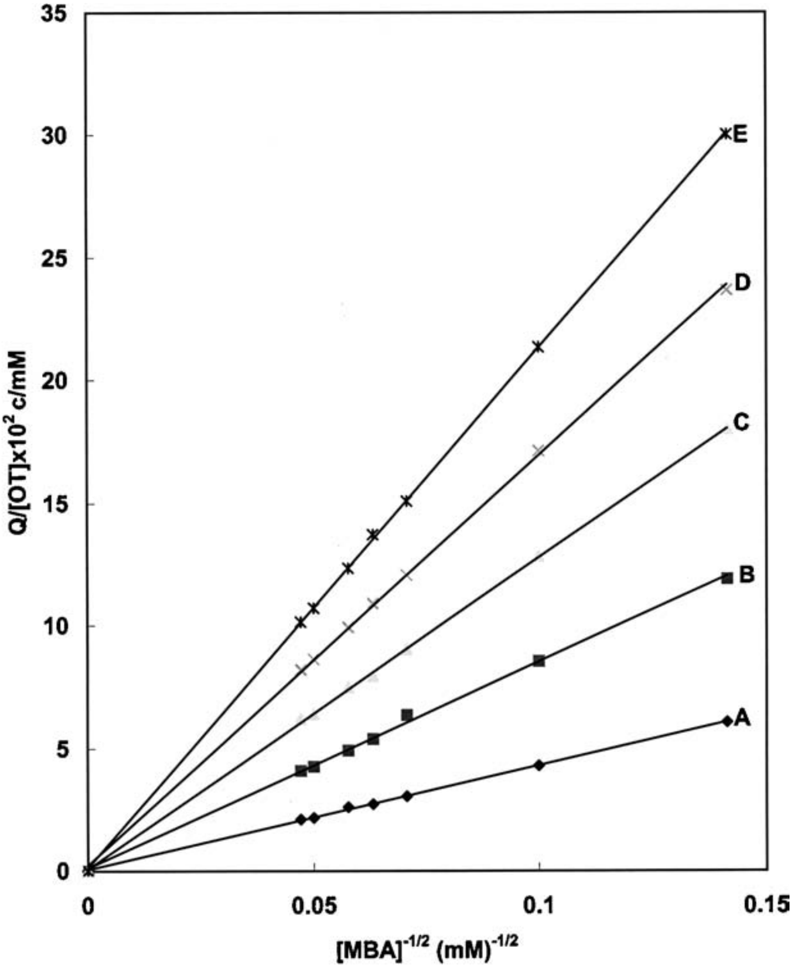


FIGURE 7 Effect of [MBA] on charge for various cycle numbers during the copolymerization of OT with MBA; scan rate = 50 mV/s. Plot A = cycle number 4; Plot B = cycle number 8; Plot C = cycle number 12; Plot D = cycle number 16; Plot E = cycle number 20.

Deducing the Growth Rate Equation for Poly(OT-co-MBA) Deposition

Attempts were also made in the current study to correlate the growth rate of poly(OT-co-MBA) deposition with experimental conditions.

TABLE II Growth rates for different ratios of [OT] and [MBA] at various cycles; scan rate = 50 mV/s

	Growth rate Q (μC, cycle^{-1}) for cycle number C_n				
Feed ratio of [OT]	4	8	12	16	20
0.1	0.28	0.28	0.27	0.27	0.27
0.2	0.57	0.57	0.57	0.56	0.56
0.3	1.32	1.30	1.30	1.30	1.29
0.4	1.78	1.78	1.77	1.77	1.77
0.6	2.39	2.38	2.38	2.38	2.38
0.8	4.49	4.49	4.48	4.48	4.48
0.9	7.16	7.15	7.08	6.97	7.13

Growth rates of poly(OT-co-MBA) were calculated for various C_n and are presented in Table II. It is interesting to note that although growth of the copolymer film exhibits an increasing trend with C_n, the growth rate is unaffected by C_n. It is also observed that the growth rate increases with increases in [OT]. In other words, the growth rate decreases with increase in [MBA]. This trend is very much similar to the growth behavior.

In order to determine the exact dependence of growth rate on C_n, [OT], and [MBA], an equation for growth rate is proposed as

$$\text{Growth rate} = \text{d(growth)/d(cycle number)} = \text{k}\,[\text{OT}]^x[\text{MBA}]^y(\text{C}_\text{n})^z \quad (4)$$

and its logarithmic form is considered

$$\log(\text{growth rate}) = \log \text{k} + x\log[\text{OT}] + y\log[\text{MBA}] + z\log \text{C}_\text{n} \quad (5)$$

As stated earlier, the growth rate is found to be independent of cycle number, so z is assigned a value of 0. Since the concentration terms [OT] and [MBA] vary simultaneously for any chosen value of C_n, several simultaneous equations were set using the values of growth rate and solved for the values of x and y. The values of x and y are thus found to be +1.0 and –0.5, respectively.

In order to establish the validity of the values of x and y, double logarithmic plots of log(growth rate $[\text{MBA}]^{1/2}$) vs. log[OT] were drawn for fixed values of C_n. These linear plots showed unit slopes (i.e.) 1.0 indicating the first power dependence of growth rate on [OT]. Direct plots of (growth rate $[\text{MBA}]^{1/2}$) vs. [OT] were made for fixed values of C_n (Figure 8). All these plots were linear with negligible intercept, confirming the value of x as 1.0.

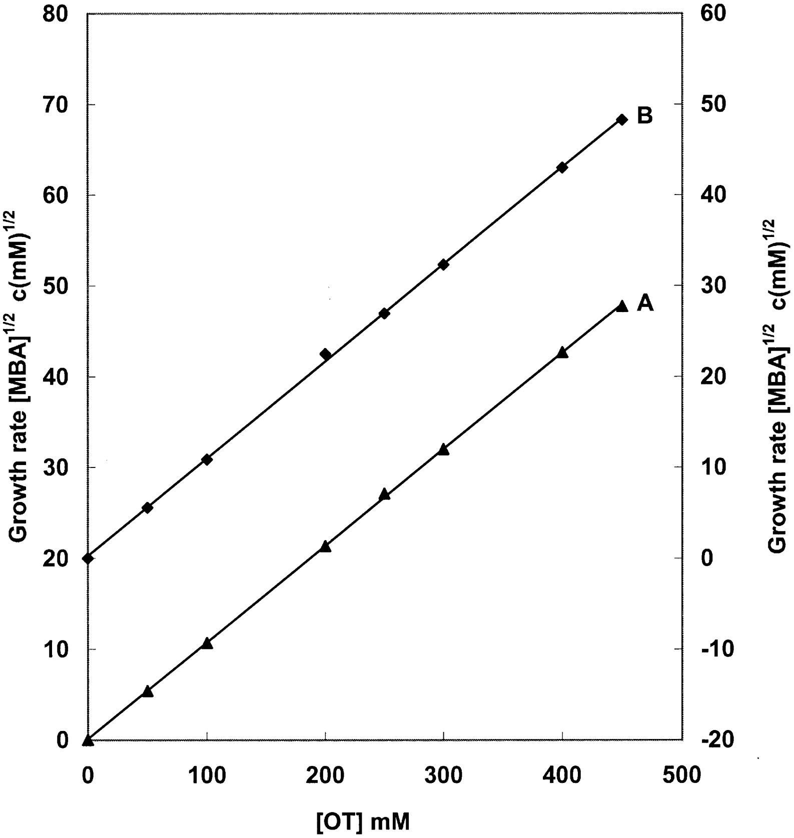


FIGURE 8 Effect of [OT] on growth rate for various cycle numbers during the copolymerization of OT with MBA; scan rate = 50 mV/s. Plot A = cycle number 8; Plot B = cycle number 16.

Using the graphically derived value of $x = 1.0$, in Equation (5), logarithmic plots of log(growth rate/[OT]) vs. log [MBA] were drawn for fixed values of C_n. These plots were linear with slope values close to –0.5. Also, direct plots of (growth rate/[OT]) vs. $[MBA]^{-1/2}$ were made for fixed values of C_n (Figure 9). All these linear plots passed through the origin and thus confirm the dependence of MBA as −0.5.

In order to ascertain the exact dependence of growth rate on experimental parameters such as C_n, [OT], and [MBA], direct plots of growth rate $[OT]^{-1}$ vs. $[MBA]^{-1/2}$ (figure not shown) for fixed C_n values were drawn. The fact that these plots are linear and pass through the origin

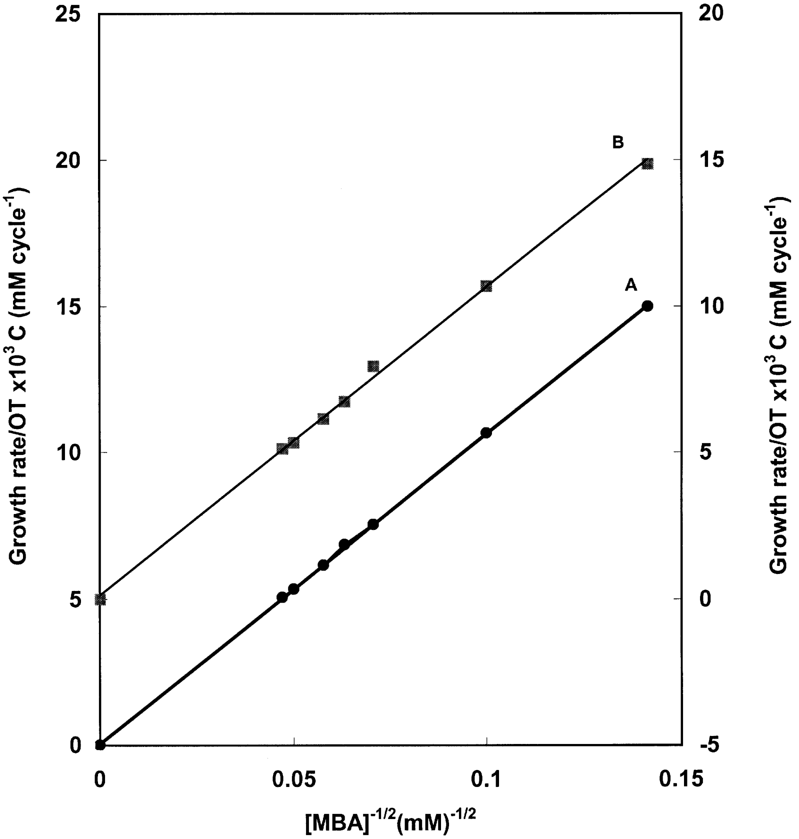


FIGURE 9 Effect of [MBA] on growth rate for various cycle numbers during the copolymerization of OT with MBA; scan rate = 50 mV/s. Plot A = cycle number 8; Plot B = cycle number 16.

confirms the first power and inverse square root dependence of growth rate on [OT] and [MBA], respectively.

Using the above experimental evidence with regard to dependence of growth rate on C_n, [OT], and [MBA], an equation for the growth rate of the copolymer deposition is given as

$$\text{Growth rate} = k[\mathrm{OT}][\mathrm{MBA}]^{-1/2} \tag{6}$$

where k is growth rate constant.

Since the experimental conditions such as scan rate and electrode surface were kept constant during copolymerization, it is now possible to interrelate the two growth parameters, namely growth and growth rate. By defining the growth rate as d(growth)/d(cycle), the growth Equation (3) can be modified as

$$\text{Growth rate} = \text{k[OT][MBA]}^{-1/2} \tag{7}$$

Equations (6) and (7), obtained by different approaches, are found to be identical, complementing the experimental evidences with regard to the dependence of growth and growth rate of the copolymer deposition. It is also inferred that the reaction rate constant k as found in Equation (7) is identical with the constant k present in Equation (6).

Determination of Growth Parameter Through Growth Function

The reaction rate constant k for the copolymerization was determined for various experimental conditions through different approaches and is presented in Tables III and IV. First, the logarithmic form of growth Equation (3)

$$\log(\text{charge}) = \log \text{k} + \log[\text{OT}] - 1/2 \log[\text{MBA}] + \log(\text{C}_\text{n}) \tag{8}$$

The approach for determining the value of k involves the calculation of the slopes (k [OT] $[\text{MBA}]^{-1/2}$) from the direct plots of charge vs. C_n

TABLE III Kinetic parameters for the electrocopolymerization of OT with MBA by cyclic voltammetry; scan rate = 50 mV/s

	log(charge)[a] vs. log C_n		Charge[b] vs. C_n	
Feed ratio of [OT]	Intercept[c]	k × 10^4 mC(mM)$^{-1/2}$ cycle^{-1}	Slope × 10^3 mC(Cycle)$^{-1}$ [d]	k × 10^4 mC(mM)$^{-1/2}$ cycle^{-1}
0.1	−0.550	1.19	0.26	1.11
0.2	−0.237	1.16	0.56	1.11
0.3	0.123	1.15	1.29	1.12
0.4	0.253	1.13	1.77	1.12
0.6	0.380	1.13	2.37	1.12
0.8	0.654	1.13	4.47	1.12
0.9	0.861	1.14	7.08	1.11

[a] log(charge) = log k + log[OT] − 1/2 log[MBA] + log(cycle number).

[b] Charge = k[OT]$[\text{MBA}]^{-1/2}$ (cycle number).

[c] log k + log[OT] −1/2 log [MBA].

[d] k[OT]/$[\text{MBA}]^{1/2}$.

TABLE IV Kinetic parameters for the electrocopolymerization of OT with MBA by cyclic voltammetry; scan rate = 100 mV/s

	$\log(Q[MBA]^{1/2})$ vs. log[OT]		$(Q[MBA]^{1/2})$ vs. [OT]		log(Q/[OT]) vs. log[MBA]		(Q/[OT]) vs. $[MBA]^{-1/2}$	
Cycle number (C_n)	Intercept[a]	$k \times 10^{4}$ [c]	slope $\times 10^{3}$ mC$(mM)^{-1/2}$ [b]	$k \times 10^{4}$ [c]	Intercept[a]	$k \times 10^{4}$ [c]	slope $\times 10^{4}$ mC$(mM)^{-1/2}$ [b]	$k \times 10^{4}$ [c]
4	−0.33	1.18	0.45	1.12	−0.36	1.11	0.45	1.12
8	−0.04	1.16	0.90	1.12	−0.06	1.10	0.90	1.12
12	0.15	1.16	1.34	1.11	0.12	1.11	1.33	1.11
16	0.23	1.18	1.76	1.10	0.23	1.06	1.74	1.08
20	0.35	1.12	2.24	1.12	0.35	1.12	2.24	1.12

Charge = $k[OT][MBA]^{-1/2}$ (cycle number).

log(charge) = log k + log[OT] − 1/2 log[MBA] + log(cycle number).

[a] log k + log[OT] −1/2 log[MBA].

[b] $k[OT]/[MBA]^{1/2}$.

[c] mC$(mM)^{-1/2}$ $(cycle)^{-1}$.

figures drawn for various feed ratios of OT and MBA. Making use of the appropriate value of [OT] and [MBA], k was evaluated.

The values of k, slopes, and intercepts are presented in Tables III and IV. The close agreement that is observed among the values of k supports the choice of Equation (3) for the growth of poly(OT-co-MBA) deposition.

Using the plots of log(Q_G $[MBA]^{1/2}$) vs. log[OT] for various C_n, the intercepts (log k + log C_n) were calculated. Substituting the values of C_n, k was evaluated. The slopes ($k \cdot C_n$) of the direct plots of (Q_G $[MBA]^{1/2}$ vs. [OT]) for various C_n were calculated, from which k was evaluated.

In a similar way, the intercepts (log k + log C_n) were calculated from the plots of log(charge/[OT] vs. log[MBA]) and k was evaluated. The slopes $k \cdot C_n$ of the direct plots of (charge/[OT]) vs. $[MBA]^{-1/2}$ (Figure 9) were also calculated. Using the respective values of C_n, k was evaluated from the slopes.

The close agreement between the values of k obtained through different approaches, as observed from Tables III and IV supports the equations assigned for the growth and growth rate of the copolymer film. The average value of the reaction rate constant k for poly(OT-co-MBA) film deposition was calculated to be 1.1×10^{-4} mC $(mM)^{-1/2}$ $(cycle)^{-1}$.

Electrochemical Behavior of Poly(OT-co-MBA) Film

Poly(OT-co-MBA) film deposited on the platinum electrode after 20 cycles of potential scanning was used for the systematic study of the electrochemical behavior of the copolymer film. The CV thus recorded for the copolymer coated electrode (using the mixture of monomers of feed ratio 0.5 each) is presented in Figure 10. A detailed analysis of the CV with regard to peak positions and peak current values was done for characterizing the copolymer film.

The CVs of the copolymer films were compared with the corresponding CVs recorded during the growth of copolymeric films for 20 cycles. The CV patterns were found to be similar in all cases. The fact that the characteristic peaks were found intact and no new peaks appeared indicates the stable nature of the copolymer films.

Dependence of Peak Potential on Scan Rate

Both the anodic and cathodic peak potentials corresponding to first and second redox processes were obtained at various scan rates for the copolymer film deposited with the mixture of monomers (for feed ratio of MBA as 0.5). It was found that all the anodic, $E_p^a(I)$ and $E_p^a(II)$, and

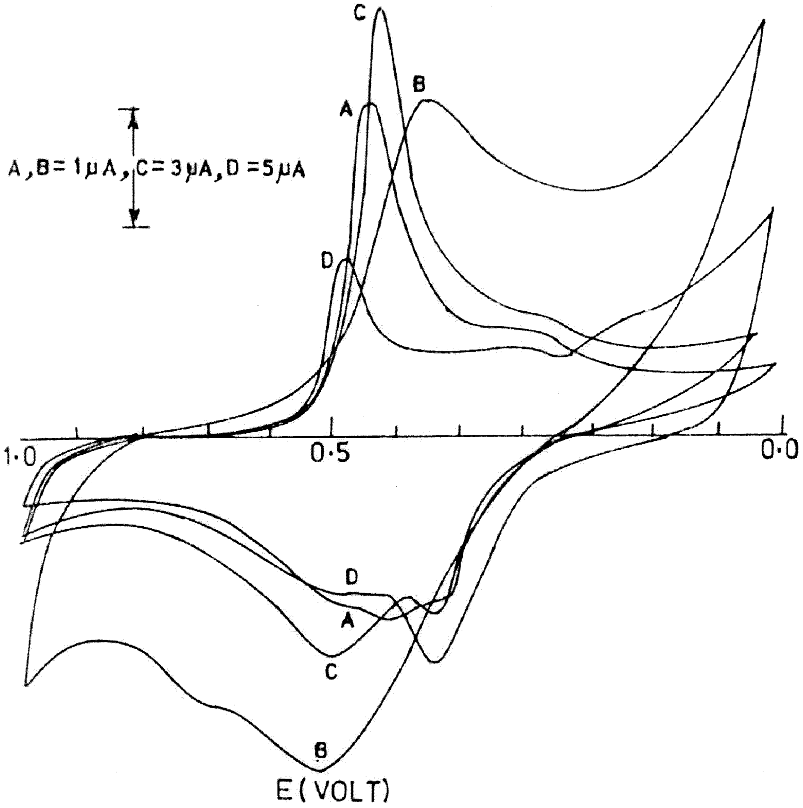


FIGURE 10 Cyclic voltammogram of electrochemically deposited poly(OT-co-MBA) films recorded at various feed ratios of [OT] and [MBA]; scan rate = 50 mV/s.

cathodic, $E_p^c(I)$ and $E_p^c(II)$, peak potentials are dependent on scan rate (ν). The anodic peak potentials, $E_p^a(I)$ and $E_p^a(II)$, show a positive shift with increase in ν, in contrast to the negative shift of cathodic peak potentials, E_p^c (I) and $E_p^c(II)$. $E_{1/2}$ for both anodic and cathodic peaks of the CV of poly(OT-co-MBA) films were measured from the CV of the copolymer film for various scan rates. It was found that the $E_{1/2}$ values do not vary much with the increase in ν.

The plots of $E_p^a(I)$ vs. $\nu^{1/2}$, $E_p^a(II)$ vs. $\nu^{1/2}$, $E_p^c(I)$ vs. $\nu^{1/2}$, and $E_p^c(II)$ vs. $\nu^{1/2}$ (not shown) were drawn for the film poly(OT-co-MBA). All these plots showed linearity. $E_{1/2}$ values of the anodic and cathodic process were determined by extrapolating these linear plots to zero scan rate. The values of $E^{a}_{1/2}$(I), $E^{a}_{1/2}$(II), $E^{c}_{1/2}$(I), and $E^{c}_{1/2}$(II) were found to be 0.130 V, 0.43 V, 0.38 V, and 0.45 V, respectively. These extrapolated values of $E_{1/2}$ are very close to the measured values, which confirms the accuracy of the experimental method. $E^{c}_{1/2}$(I) is higher by 180 mV when compared with the $E^{c}_{1/2}$(I) values obtained for POT film, $E^{c}_{1/2}(I) = 0.20$. Other values of $E_{1/2}$ of the copolymer exhibit a small change in the range 0.2–0.7 V in comparison with that of the POT film, $E^{a}_{1/2}(I) = 0.27$ V, $E^{a}_{1/2}(II) = 0.5$ V, and $E^{c}_{1/2}(II) = 0.47$ V.

It is not possible to compare the $E_{1/2}$values for the homopolymers with those of the copolymer because MBA monomers themselves do not give a polymeric film on electropolymerization. But it is clearly seen that when compared to $E_{1/2}$ values of POT (0.27 V, 0.50 V) the new polymeric material poly(OT-co-MBA) has different values (0.30 V, 0.43 V) for the first and second anodic processes. A mixture of two homopolymers is not possible here. Therefore, the fact that a copolymer was obtained seems to be well supported in this case.

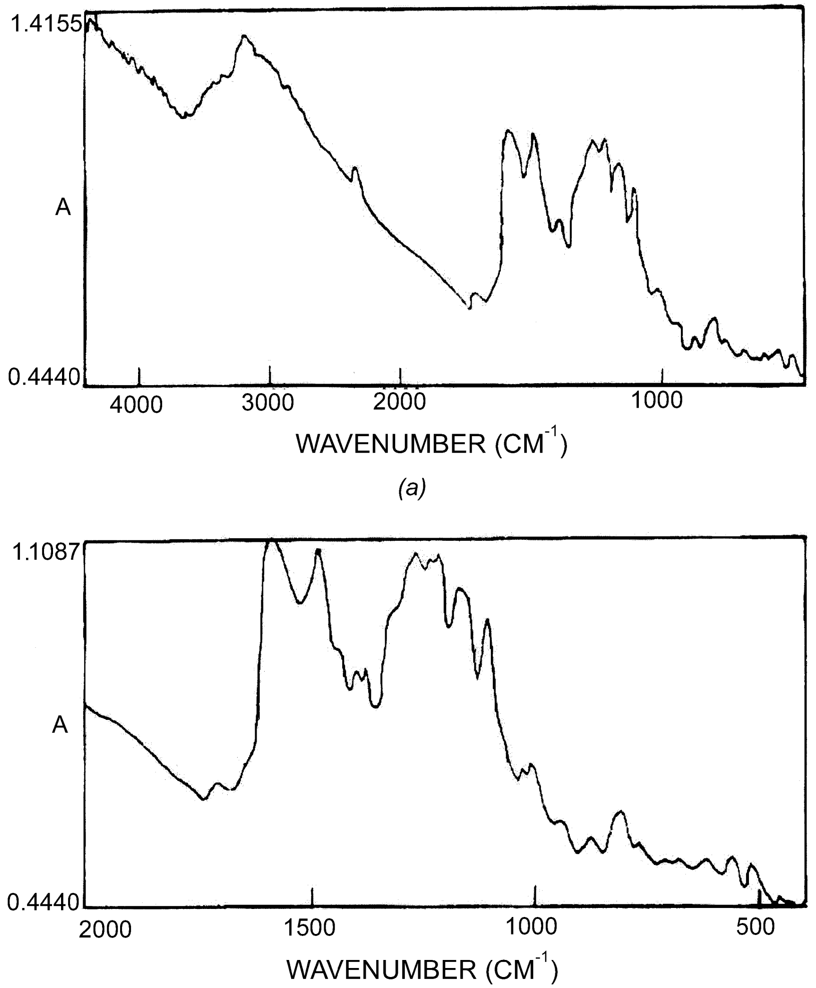
Chemical Polymerization of Poly(OT-co-MBA)

In order to ascertain the characteristics of poly(OT-co-MBA), copolymerization of OT with MBA was carried out by the method of controlled chemical oxidation. The copolymer poly(OT-co-MBA) was chemically synthesized using the oxidant potassium peroxodisulfate in acidic aqueous medium.

FT-IR Spectroscopy

The FT-IR spectrum recorded for the copolymer sample in the range of 450–4400 cm^{-1} is presented in Figure 11.

The prominent infrared absorptions for this copolymer appear at wave numbers 1595, 1480, 1250, 1220, 1175, 1108, and 805 cm^{-1}. The absorption pattern is not significantly different from that of poly(OT-co-MCA) except for the twin peaks at 1595 and 1480 cm^{-1}. The relative intensities of the two peaks show a change from the other spectra. While the higher frequency peaks are less intense in the case of POT and copolymers having OCA and MCA, the two peaks are of equal intensity in this case. The 1595 and 1480 cm^{-1} peaks can be assigned to the quinoid and benzenoid ring deformations due to $C{=}N$ and $C{-}N$ bonds, respectively. The relative intensities should normally depend on the oxidation state[20]. It is difficult to see any reason why bromoaniline addition should lead to higher oxidation. One other possible factor may be cross-linking or the



(a)

(b)

FIGURE 11 FT-IR spectrum of poly(OT-co-MBA). (a) Wavenumber in the region (4400–450 cm^{-1}), (b) wavenumber in the region (2000–450 cm^{-1}).

increase in inter-chain distance because of the bulky bromine atoms on the chain. It may be noted that on substitution with the large size N-pentylaniline, the polymer formed showed an increased intensity of the higher frequency peak[21].

UV-Visible Spectroscopy

Figure 12 shows the UV-visible spectrum of poly(OT-co-MBA). It exhibits a well defined peak at 283 nm and a broad band at 554 nm, which corresponds to π-$\pi^\star$ transition of the benzenoid rings in the polymer backbone and polaronic excitation of benzenoid to quinoid, respectively[22, 23].

The large hypsochromic shift at 283 nm from the 310 nm peak of POT may be due to the electron withdrawing nature of the bromo groups in the polymer backbone. The steric hindrances due to bromine inducing deformation along the chain and consequent decrease in the degree of

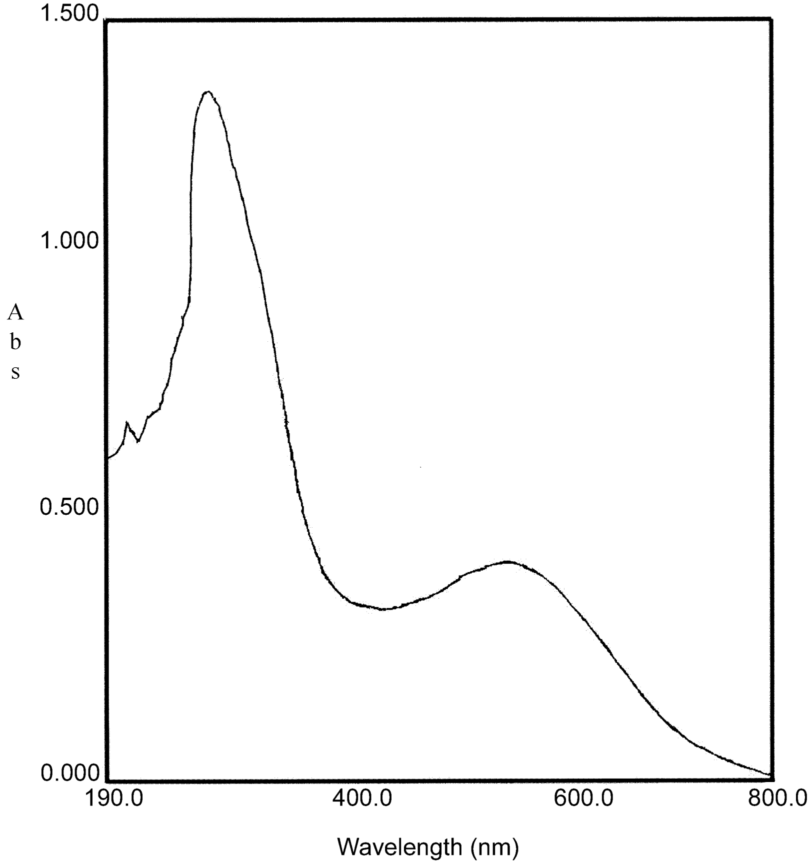


FIGURE 12 UV-visible spectrum of poly(OT-co-MBA).

conjugation also may play a role in shifting the absorption to higher frequencies.

CONCLUSIONS

Electrochemical polymerization of OT and MBA and copolymerization of OT with MBA were performed by cyclic voltammetry under different experimental conditions. CV was used to monitor the growth behavior of copolymeric films. A growth equation relating the experimental conditions of copolymerization and charge associated with film deposition was obtained as $\mathrm{Growth} = \mathrm{k[OT][MBA]}^{-1/2}$. The growth rate constant k was evaluated as 1.1×10^{-4} mC $(\mathrm{mM})^{-1/2}$ $(\mathrm{cycle})^{-1}$. The FT-IR and UV-visible spectroscopic results revealed significant differences between the homopolymers and copolymer.

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